

1917
J764

Jordan

Observations on the Rare Earths:

A Study of Some Methods for the Separation of
Gadolinium

OBSERVATIONS ON THE RARE EARTHS:
A STUDY OF SOME METHODS FOR THE SEPARATION
OF GADOLINIUM

BY

LOUIS JORDAN
A. B. Bates College, 1915

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF ARTS

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1917

1917
J764

UNIVERSITY OF ILLINOIS
THE GRADUATE SCHOOL

May 28 1917

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY _____ LOUIS JORDAN _____
ENTITLED _____ OBSERVATIONS ON THE RARE EARTHS; A STUDY OF _____
_____ SOME METHODS FOR THE SEPARATION OF GADOLINIUM _____
BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF _____ MASTER OF ARTS _____

B. S. Hopkins

In Charge of Thesis

W. A. Noyes

Head of Department

Recommendation concurred in:*

Committee

on

Final Examination*.

*Required for doctor's degree but not for master's.

376539

8 Feb. 17 Ciley

ACKNOWLEDGEMENT

The writer wishes to express his appreciation to Dr. C. W. Balke for the introduction to the study of the rare earths and to Dr. B. S. Hopkins for his kindly guidance and interest during the progress of this work.



Digitized by the Internet Archive
in 2013

<http://archive.org/details/observationsonra00jord>

TABLE OF CONTENTS

- I. Introduction
- II. History of Gadolinium
- III. Sources of Material
- IV. The Determination of Equivalents
- V. Fractional Crystallization of Di-methyl Phosphates
- VI. Fractional Crystallization of the Bromates
- VII. Fractional Precipitation with Sodium Glycolate
- VIII. Summary

I. Introduction

The object of this work was to study some methods for the separation of gadolinium from rare earth mixtures and for the purification of gadolinium rich material with the view of obtaining gadolinium of a fairly high degree of purity.

II. History of Gadolinium

The discovery of gadolinium, first designated as $Y\alpha$, among the earths of Samarskite, was announced by C. Marignac¹ in the year 1880. Those earths from Samarskite whose nitrates were most stable on fusion, were divided into four fractions by precipitation with potassium sulfate. The most soluble of these fractions, number I, contained the yttrium, the two least soluble, III and IV, the didymium. Fraction II contained an earth whose solution showed no absorption lines and whose oxide was a pale yellow orange color. The equivalent of this earth ($RO = 119-120$) was a maximum of the equivalents of the earths on either side in the potassium sulfate fractionation. This fact indicated a new earth and the high equivalent distinguished it from yttrium. By fusion of the nitrates of this oxide, Marignac found that the terbium nitrate was less stable than that of gadolinium and in this manner he removed some of the terbium from his new oxide. This behavior distinguished the new earth from ytterbium whose nitrate decomposes before terbium nitrate on fusion. The equivalent of this purified earth was 120.5 or $Gd = 156.75$.

The name gadolinium was given to this new earth some six years

¹Ann. chim. phys., (5) 20, 535(1880)

after its discovery¹. The name was given in honor of John Gadolin, who first recognized the presence of rare earths in the mineral gadolinite, also named in his honor.

The development of methods for separating gadolinium is easily traced by a study of the methods of purification employed in the various determinations of the atomic weight of the element. The list of these determinations, with the values obtained recalculated, is given in F. W. Clarke's ''A Recalculation of the Atomic Weights''². A similar review of these determinations is also given by Brauner³.

In 1890 Lecoq de Boisbaudran⁴ published the results of some work on a small amount (1.5 g.) of gadolinium oxide sent him by Marignac. Fractional precipitation of this material with dilute ammonium hydroxide concentrated the samarium in the ''head'' fractions and the didymium in the ''tail'' fractions. In the two fractions last to precipitate, the oxide was yellowish white, containing didymium and a little terbium and samarium as impurities in the gadolinium. Determination of the equivalent of this material by converting a known weight of the oxide to the sulfate, gave the value 154.82⁵ as the average atomic weight of the earth.

In 1892 Bettendorf⁶ announced the separation of gadolinium from earths from the mineral orthite. The original mixture of the earths contained didymium, samarium, gadolinium and terbium. The

¹Boisbaudran, Compt. rend., 102, 902(1886); Chem. News, 53, 225.

²Smithsonian Miscell. Collec., Vol. 53, No. 3, The Constants of Nature, Part V, p. 530.

³Abegg's Handbuch, Bd. 3, Abth. 1, p. 303.

⁴Compt. rend., 111, 394, 409(1892)

⁵Values given in this paper for atomic weights are the recalculated values as given by F. W. Clarke.

⁶Annalen, 263, 167(1891); 270, 376(1892)

didymium was separated by the fusion of the nitrates and the mixture of samarium, gadolinium and terbium was then treated with a saturated solution of potassium sulfate and a great part of the samarium precipitated out as the slightly soluble potassium samarium sulfate. The earth remaining in solution gave a yellowish red oxide and had an equivalent $RO = 119.96$. This contained terbium and gadolinium with a very little samarium. The nitrate solution of this yellowish red oxide was fractionally precipitated with dilute ammonium hydroxide. The samarium and gadolinium concentrated in the fractions last to precipitate. These last fractions were treated with potassium sulfate solution to remove the samarium. The determination of the atomic weight of the earth in the fractions thus purified gave the value, $Gd = 156.75$. The oxide is described as a faint yellow. Bettendorf observed that when the oxide was heated gently in an atmosphere of hydrogen, it became colorless without change of weight, but when strongly ignited in hydrogen it seemed to undergo partial reduction, assuming a faint greyish hue.

In 1900 Benedicks¹ obtained a fairly pure oxide of gadolinium by the fractional crystallization of the simple nitrates in nitric acid, gadolinium nitrate being the least soluble of all the rare earth nitrates². This material, further purified by precipitation with dilute ammonia, was used for determining the atomic weight of gadolinium. The mean value of six determinations gave $Gd = 156.52$.

Demarcay³, by fractional crystallization of the double magnesium nitrates of the rare earths in order to separate europium from the terbium earths, obtained some gadolinium magnesium nitrate that was

¹Z. anorg. Chem., 22, 393(1900)

²Demarcay, Compt. rend., 122, 728(1895)

³Compt. rend., 131, 343(1900)

quite pure material. It gave an oxide having only a slight yellow color. Demarcay states that the atomic weight of the earth was ''in the neighborhood of 155.''

The next attempt to purify gadolinium was that of Marc¹. By a considerable number of fractional precipitations with potassium sulfate and dilute ammonia, Marc obtained a small amount of a slightly yellowish oxide, free from neodymium and samarium, having an atomic weight of 156.39.

Brauner², in his review of the atomic weight determinations of gadolinium, lists one determination by himself, but gives no details as to the methods used in the purification of the material which he had received from Cleve³. The values obtained were 155.725 and 155.78.

In 1903 and 1904 Urbain and Lacombe⁴ described the fractional crystallization of the double magnesium nitrates of the terbium earths with the addition of the isomorphous bismuth magnesium nitrate. The solubility of the bismuth magnesium nitrate was found to lie between that of the double nitrates of samarium and europium, making possible a rather sharp separation at that point in the series. Long continued fractionation served to concentrate the europium in the fractions slightly more soluble than the bismuth magnesium nitrate and the gadolinium and terbium in the fractions at the soluble end of the series. These most soluble fractions, containing mostly gadolinium with a little europium and terbium, were further purified by Urbain⁵ thru the recrystallization of the

¹Z. anorg. Chem., 38, 121(1904)

²Loc. cit.

³F. W. Clarke, Loc. cit.

⁴Compt. rend., 137, 792(1903); 138, 84, 627(1904)

⁵Ibid, 140, 583(1905)

double nickel nitrates in strong nitric acid. He found that this treatment rapidly removed the terbium in the most soluble fractions. At the completion of the fractionation only the last four fractions at the soluble end of the series gave slightly yellow colored oxides, the remaining fractions giving perfectly white oxides. The six fractions at the insoluble end of the series gave approximately constant values for the atomic weight, ten determinations on the material from these six fractions giving an average value of $Gd = 157.24$. The fractions colored slightly yellow also gave an atomic weight very close to this same value, from 157.04 to 157.45.

The atomic weight determination of Feit and Przibylla¹ represents no new purification of gadolinium. They simply applied their volumetric method to material obtained from Urbain. They give the value $Gd = 157.388$.

Brauner² points out that apparently all the gadolinium prepared by workers up to the time of Urbain's work, contained some earth of atomic weight less than 157 and that the best of all the early determinations is the very earliest of all, that of Marignac.

III. Sources of Material

The material for the present work came in part from cerium group earths, in part from yttrium group earths. Europium, gadolinium and terbium form a transition group between the earths of the cerium and yttrium groups, these three earths often being designated as the terbium group. In the usual separation of the cerium and yttrium earths with potassium or sodium sulfate, the gadolinium is

¹Z. anorg. Chem., 50, 249(1906)

²Loc. cit.

divided between the two groups. It follows that either or both groups may be taken as the source of gadolinium material.

The gadolinium material from cerium group sources was taken from fractions 13 to 18 of a double magnesium nitrate series with bismuth magnesium nitrate that had been run for some time by other workers in this laboratory. These fractions were more soluble than those containing the bismuth and the absorption spectrum showed weak lines of samarium. After removal of the bismuth and magnesium, these six fractions gave about 200 g. of an orange brown oxide. A concentrated solution of this oxide in nitric acid showed a very distinct absorption spectrum of samarium and a faint but distinct line of europium at 525. The color of the oxide indicated the presence of terbium altho no terbium absorption was observed. The average atomic weight of this material, determined by the potassium permanganate titration method as described below, was 157.20. While the accepted value for gadolinium is 157.3, this material was not as pure gadolinium as the atomic weight might at first indicate. The chief impurities, samarium (at. wt. 150.4) and terbium (at. wt. 159.2), tend to neutralize each other. Some of this orange brown oxide was ignited in an atmosphere of hydrogen to make certain that the color was due to the presence of terbium. It is usually stated that a white oxide colored brown by a small amount of terbium will become pure white on igniting in hydrogen. Strong ignition of this oxide in hydrogen changed the color to a distinct gray, not white. But more gentle heating in hydrogen gave a perfectly white oxide. This behavior of gadolinium oxide containing a small amount of terbium was first noted by Bettendorf¹.

¹Loc. cit.

Gadolinium material from yttrium earths was obtained by combining the least soluble fractions from five bromate series. Two of these series were composed of material from which the cerium earths had been removed by precipitation with potassium sulfate. The other three series were made up of earths as extracted from the mineral gadolinite without any treatment to remove cerium group elements. The insoluble end from each of these series, therefore, contained in addition to the gadolinium, a considerable amount of neodymium, less prae-seodymium and some samarium. The fractions from all five series, twelve fractions in all, were combined into two fractions according to the depth of the red (neodymium) color and by comparison of the absorption spectra, the lighter red fraction being the richer in gadolinium and containing samarium, the deeper colored fraction containing a considerable amount of neodymium and some holmium and dysprosium. These two fractions together contained the equivalent of about 250 g. of earth oxides. The oxide from Fraction 1 was orange brown, that from Fraction 2 a dark orange brown. The atomic weights for these fractions were determined: Fraction 1, 154.36; Fraction 2, 152.9.

IV. The Determination of Equivalents

The method of Feit and Przibylla¹ for the determination of the atomic weights was tried but was not found as convenient as the potassium permanganate titration method of Gibbs². This latter method was the one used in determining values for the atomic weights of earths in this work.

¹Loc. cit.

²Am. Chem. J., 15, 546(1893)

This method consists of the following procedure: The earth oxalate is precipitated from a hot, dilute solution of the nitrates or chlorides by the addition of a hot solution of oxalic acid which had been carefully purified by recrystallization and centrifugal drainage of C.P. acid. The finely crystalline oxalates thus obtained were washed to completely remove any oxalic acid, dried for several hours at 110-115° C., thoroly ground and two samples weighed out. One sample was ignited to the oxide; the other was dissolved in an excess of 5 N sulfuric acid, diluted, and the oxalic acid thus liberated titrated with 0.1 N potassium permanganate. The atomic weight of the earth, R , was then calculated by the formula, $R = \frac{108 \times \%R_2O_3}{\%C_2O_3} - 24$. The titration was carried out in a hot solution. The method is very accurate, enabling checks within a tenth of a unit in the atomic weight.

V. Fractional Crystallization of Di-methyl Phosphates

The fractionation of the rare earth di-methyl phosphates was suggested as a method of value in the separation of gadolinium by James and Morgan¹ as a result of their work on some crude gadolinium material. They state that comparatively pure gadolinium, judging by the light color of the oxide, was obtained in a very short time. These authors give the order of increasing solubility of the earth di-methyl phosphates as Yb, Er, Y, Gd, Sm, Nd, Pr, Ce and La. This order is the reverse of the more usual one in which lanthanum is at the insoluble end and ytterbium one of the most soluble of all the earths. Further, the earth di-methyl phosphates are very much less soluble in water at 80-90° C. than at ordinary temperatures.

¹Jour. Am. Chem. Soc., 36, 10-16(1914)

Di-methyl phosphoric acid was prepared as suggested by James according to the method of Hugo Schiff¹. In a 2 l. Jena Florence flask, fitted with a three hole rubber stopper, was placed 125 cc. of phosphorus oxy-chloride. A separatory funnel containing 156 cc. of methyl alcohol passed thru the stopper of the flask and the alcohol was slowly run into the reaction flask. A glass tube reached to the bottom of the flask, into the liquid, thru which air was forced slowly during the reaction to keep the mixture stirred and to force out thru a second tube and into a beaker of water, the methyl chloride and hydrochloric acid formed by the reaction. Running water kept the contents of the flask cool during the reaction.

At the completion of the reaction, the mixture, after dilution and warming to complete the removal of any remaining methyl chloride and hydrochloric acid, was neutralized with barium carbonate. The precipitate of barium orthophosphate was filtered off and the clear solution of barium di-methyl phosphate treated with just sufficient sulfuric acid to precipitate the barium. The clear filtrate of di-methyl phosphoric acid was used for dissolving the earth oxides.

The material converted to the di-methyl phosphates was about 33 g. of the oxide described above as obtained from cerium group earths in a double magnesium nitrate series. The earth oxide was added to a dilute solution of the di-methyl phosphoric acid and went into solution in the cold with a little shaking. This solution was heated on the steam bath to 80° C. A small quantity of a gelatinous precipitate formed which was insoluble on cooling the solution. This precipitate was filtered off. The solution was again heated till a precipitate formed, this time entirely soluble

¹Chem. Centralblatt, (1857), 761-63.

on cooling the solution, showing it to be earth di-methyl phosphates. This solution was then evaporated till a crop of crystals of sufficient size for the first fraction had formed, the liquid poured off, again evaporated to crystallization and the first crop of crystals dissolved in cold water to form Fraction 1. The solution was divided into six fractions. This series was run in the following manner: The fractions were heated gradually to 80° C. on a steam or water bath with frequent stirring, the earth di-methyl phosphates crystallizing out nicely. When sufficient precipitate had formed, the fraction was heated for a few minutes without stirring in order that the crystalline precipitate might form a more compact mass that would allow better draining of the liquor from the crystals in pouring the fractions. The fractions were poured while still hot, the mother liquor being strained thru an ordinary Gooch crucible (without asbestos) into the next more soluble fraction. Loose crystals of the earth di-methyl phosphates in the liquid were thus retained in the bottom of the crucible and returned to the fraction from which they were poured. The fractions were then set aside and on cooling the crystals went entirely into solution.

The progress of the fractionation could be judged from the absorption spectrum of the cold saturated solutions of the fractions. After only three series of fractionations the most soluble fraction was a light yellow and showed quite distinct lines of samarium. As the fractions at the insoluble end became too small for convenient fractionation they were set out of the series. After fifteen series of crystallizations had been carried out the fractions remaining were numbered 6 to 12.

These fractions were diluted and the earths precipitated as

oxalates from a hot solution strongly acid with nitric acid, the oxalates dried and ignited to the oxides. The oxide was then taken up in nitric acid and again precipitated as oxalate to make certain of the removal of all phosphates. The strong nitric acid solution of the oxide before the second precipitation was observed for absorption spectrum. The lines observed compared with those observed in the saturated di-methyl phosphate solution and it is these latter that are referred to below in Table I. The atomic weights of the material in these fractions were determined in the usual manner.

Table I

Di-methyl Phosphate Fractionation

Fract. No.	Wt. of oxide	Color of oxide	Color sol. $R_2(Me_2PO_4)_6$	Absorp. shows	At. wt.
1	0.20 g.	Dark or. brn.	White	-----	
2	0.40	" " "	"	-----	
3	0.25	" " "	"	-----	157.98 ¹
4	0.74	" " "	"	-----	
5	0.72	Orange brn.	"	-----	
6	0.65	Light or. brn.	"	-----	
7	4.58	" " "	"	No abs.	157.46
8	4.95	Light yel. brn.	"	Sm(barely visible)	157.27
9	4.73	" " "	"	Sm(very faint)	157.25
10	4.29	" " "	Faint yel.	Sm(faint)	157.29
11	3.90	Cream color	Yellow	Sm(distinct)	156.94
12	6.00	" "	Golden yel.	Sm(strong) Eu(sharp)	156.41

¹Fractions 1, 2 and 3 were combined for the atomic weight determination given under Fraction 3.

The dark orange brown color of the oxides at the insoluble end of this series indicates the concentration of terbium in the least soluble fractions as does also the atomic weight, considerably higher than that of the original oxide, 157.20. The value 157.98 for Fraction 3 corresponds to a 3% content of terbium. The light color of the oxide of Fraction 12 shows the absence of any considerable amount of terbium and the strong absorption lines indicate the concentration of samarium and europium in this fraction. The atomic weight of the most soluble fraction, 156.41, corresponds to about 12% samarium.

Fractions 8, 9 and 10 showed only faint absorption lines for samarium at 465 and 475, the two strongest of the samarium lines. This fact, together with the light color of the oxide as compared with the original material, would seem to indicate that these oxides contained only small amounts of either samarium or terbium. A better indication of the purity of the material is the practically constant atomic weight of these three successive fractions, leading to the conclusion that there was no longer any separation of earths of different atomic weights by this method of fractionation. The constant atomic weight of these fractions and the closeness of the value obtained to the present accepted value for gadolinium (157.3) indicate a fairly high degree of purity in this oxide. It should be pointed out, however, that it was the experience of Hopkins and Balke¹ that the determination of equivalents of yttrium material by the potassium permanganate method gave values for the atomic weight that were about 0.5 of a unit lower than the values obtained on the same material by a careful application of the oxide-chloride ratio.

¹Jour. Am. Chem. Soc., 38, 2332(1916)

VI. Fractional Crystallization of the Bromates

James and Bissell¹ found that the fractional crystallization of the bromates gave them a rapid concentration of terbium in the fractions more soluble than the neodymium bromate. A white oxide of gadolinium was obtained from the fractions less soluble than the neodymium. With this in mind, the material described above as from yttrium group sources was fractionated as the bromates. As before stated, this material contained a considerable amount of neodymium. It was hoped that by its concentration between the terbium and gadolinium, it would be possible to remove from the oxide taken the terbium that was present in amounts sufficient to color the oxide orange brown.

The two original fractions of bromates were made into a series of 10 to 12 fractions and carried thru some fifty series of crystallizations. The fractions at the completion of the work were numbered 14 to 29. Table II shows the composition of these fractions as determined by the absorption of the saturated solution of the bromates.

Fractions 18 to 22 were selected as those probably containing the best gadolinium material. The most of the samarium was in the fractions less soluble than the neodymium with the dysprosium and terbium in the more soluble fractions. The earths were recovered from the fractions as the oxides according to the method described by Engle and Balke².

Fraction 20 was converted to the sulfate and treated with a saturated potassium sulfate solution in the attempt to remove some

¹Jour. Am. Chem. Soc., 36, 2060(1914); 38, 873(1916)

²Ibid, 39, 53(1917)

of the samarium and neodymium still present in the oxide. The atomic weight of the material thus treated showed a small rise, 155.94 as compared with 155.57 of the original Fraction 20. The absorption of the purified portion of Fraction 20 still showed neodymium but only very faint indications of samarium even in a concentrated solution of the nitrates.

The oxide from this purified material was lighter colored, more nearly white, than the oxides from those fractions of the di-methyl phosphate series that were considered to contain the most pure gadolinium. This indicated that the bromate fractionation was the more efficient of the two methods in removing the last traces of terbium. The small amount of neodymium and samarium present is more easily removed from gadolinium than the last traces of terbium.

Table II

Fractionation of Bromates				
Atomic weight of original material: Fract. 1, 154.36				
Fract. 2, 152.9				
Fract. No.	Color of Bromates	Absorption shows	Color of oxide	Atomic weight
14	Light yellow	Sm		
15	" "	Sm		
16	Nearly colorless	Sm Nd	Pale cream	
17	" "	Sm Nd		
18	Flesh color	Nd Sm	Cream	
19	" "	Nd Sm		
20	Pale pink	Nd Sm	Cream	155.57
21	" "	Nd Sm Dy		
22	" "	Nd Dy Sm	Light or. brn.	
23 to 29	Pink to Red	Nd Pr Dy Ho		

VII. Fractional Precipitation with Sodium Glycolate

Jantsch and Grünkraut¹ studied the rare earth glycolates and determined the solubilities of a number of these salts. The order of increasing solubility is given as: Y, La, Ce, Pr, Nd, Sm and Gd. The gadolinium glycolate was found to be more than twice as soluble as the samarium glycolate, the next most soluble. These authors also studied the fractional precipitation with sodium glycolate of a mixture of earths containing Pr, Nd, Sm, Ho, Y, and Er and obtained a marked separation. Because of the very great solubility of gadolinium glycolate in comparison with the other earths, it was decided to try the precipitation with sodium glycolate on some of the gadolinium material from the same source as that used for the study of the di-methyl phosphates.

Sodium glycolate was prepared in the following manner, according to the method of Holzer²: 50 g. of monochloroacetic acid was dissolved in 400 cc. of water and 56 g. of calcium carbonate added gradually. The flask containing the mixture was heated on the steam bath for nearly 48 hours, the level of the water being kept constant. The clear solution was decanted from the precipitate at the bottom and on standing a short time the liquid crystallized out a jelly-like mass of calcium glycolate. This was dried on a Buchner funnel with suction and then extracted several times with a small amount of water to remove the greater part of the calcium chloride. The precipitate remaining in the flask was boiled up with water to extract the remainder of the calcium glycolate and

¹Z. anorg. Chem., 79, 305(1913)

²Ber., 16, 2955(1883); also L. Vanino, Handbuch d. Prap. Chime, Bd. II, p 126.

treated as the first solution. The calcium glycolate thus obtained was dissolved in hot water and oxalic acid added in just sufficient quantity to precipitate nearly all of the calcium and the acid filtrate just neutralized with sodium hydroxide.

A neutral solution of the nitrates of the gadolinium rich oxide was prepared by dissolving the original oxide in nitric acid, precipitating the earths as hydroxides with ammonium hydroxide, washing thoroly, and carefully dissolving up these hydroxides suspended in water by the addition of nitric acid. The solution could be neutralized by the addition of dilute sodium hydroxide if too much acid were used. A drop of methyl orange was added to the earth nitrate solution and also to the sodium glycolate solution in order to be certain that the solutions were entirely neutral. The earth nitrate solution was diluted till it contained about 8 g. of earth oxide in a liter.

To the hot solution of the nitrates the sodium glycolate solution was added. If both solutions were entirely neutral, the addition of the sodium glycolate formed a cloudiness just as it mixed with the nitrate solution but this precipitate dissolved almost immediately. As more of the glycolate solution was added this first precipitate dissolved more and more slowly. When the turbidity was permanent, some excess of the sodium glycolate was added and the whole solution heated for about an hour on the steam bath. On removing and cooling an exceedingly fine granular precipitate settled nicely to the bottom of the flask. This precipitate filtered easily and was dried and ignited directly to the oxide. A second precipitate was removed in the same manner, but

the third addition of sodium glycolate failed to produce any further precipitate. The remaining solution was acidified with nitric acid and the rest of the earths precipitated with oxalic acid. By far the greater part of the earths was obtained in this last fraction. There was almost no difference in the color of the oxides from these three fractions, all equally orange brown. Hence there was little if any concentration of the terbium by this method, but the atomic weight of the first fraction showed a rapid concentration of samarium. Samarium lines were only barely visible in the absorption of a concentrated nitrate solution of Fraction 3. The constant atomic weight of Fractions 2 and 3 indicate practically complete removal of samarium. The atomic weight of Fraction 1 corresponds to the presence of about 8% samarium.

Table III

Precipitation with Sodium Glycolate

Atomic weight original = 157.20

Fraction No.	Absorption Shows	Atomic Weight
1	Sm	156.70
2		157.47
3	Sm(barely visible)	157.46

VIII. Summary

1. The di-methyl phosphate fractionation very rapidly and completely concentrated the europium and samarium and removed them from the gadolinium. The most of the terbium was separated in the insoluble fractions of the series. The method did not remove the last traces of terbium that still colored the gadolinium oxide a light yellow brown. Gadolinium oxide of considerable purity was obtained from the middle fractions of this series.

2. Gadolinium material giving an oxide colored orange brown by terbium was fractionated as the bromates in the presence of neodymium. The method was more tedious than the di-methyl phosphate method but almost completely removed even the last traces of terbium from the gadolinium and furnished a light cream, almost colorless, oxide. This oxide still contained a small quantity of neodymium and samarium. The first method studied would seem to be an effective method for removing these earths.

3. Precipitation of a neutral nitrate solution of the earths with sodium glycolate rapidly removed samarium from gadolinium but did not appreciably concentrate the terbium.

4. The above results suggest the following procedure for the separation of gadolinium from rare earth mixtures: The cerium should be removed by the potassium bromate method and the mixed rare earths fractionally crystallized as the bromates without having been separated into the cerium and yttrium groups. The insoluble end of the bromate series will contain only europium, samarium, gadolinium and neodymium. These fractions may be converted to the di-methyl phosphates and fractionated. The gadolinium should be

easily obtained very pure from the least soluble fractions.

Precipitation with sodium glycolate may take the place of the di-methyl phosphate fractionation or may be employed for the removal of the last traces of samarium remaining in the gadolinium from the di-methyl phosphate series.

UNIVERSITY OF ILLINOIS-URBANA



3 0112 082199230